(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
17 April 2003 (17.04.2003)

PCT

(10) International Publication Number
WO 03/031323 A1

(51) International Patent Classification[7]: B82B 3/00

(21) International Application Number: PCT/KR02/00101

(22) International Filing Date: 22 January 2002 (22.01.2002)

(25) Filing Language: Korean

(26) Publication Language: English

(30) Priority Data:
2001/63077 12 October 2001 (12.10.2001) KR

(71) Applicant *(for all designated States except US)*: **KOREA NANO TECHNOLOGY CO., LTD.** [KR/KR]; 402 Sekwang Building, #1706-4 Seocho-dong, Seocho-gu, Seoul 137-070 (KR).

(72) Inventor; and
(75) Inventor/Applicant *(for US only)*: **HYEON, Taeg-Hwan** [KR/KR]; No. Ga-204 Professor Apt., #242-2 Bongcheon7-dong, Gwanak-gu, 151-057 Seoul (KR).

(74) Agent: **LEE, Young-Pil**; The Cheonghwa Bldg, 1571-18 Seocho-dong, Seocho-gu, Seoul 137-874 (KR).

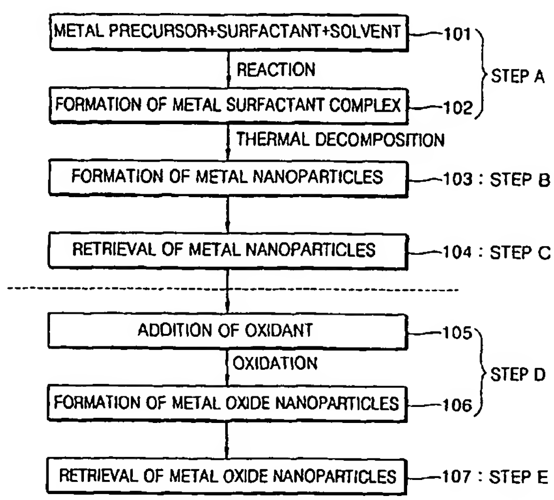
(81) Designated States *(national)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(84) Designated States *(regional)*: ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) **Title:** SYNTHESIS OF MONO-DISPERSE AND HIGHLY-CRYSTALLINE NANO-PARTICLES OF METALS, ALLOYS, METAL OXIDES, AND MULTI-METALLIC OXIDES WITHOUT A SIZE-SELECTION PROCESS



(57) **Abstract:** A synthetic method of fabricating highly crystalline and monodisperse nanoparticles of metals, multi-metallic alloys, monometallic oxides and multi-metallic oxides without a size selection process are disclosed. A typical synthetic method comprises the steps of, synthesis of a metal surfactant complex from the reaction of a metal precursor and a surfactant, high temperature thermal decomposition of the metal surfactant complex to produce monodisperse metal nanoparticles, and completing the formation of synthesized metal, metal alloy or metal oxide nanoparticles by adding a poor solvent followed by centrifuging. For obtaining highly crystalline monodisperse nanoparticles, additional steps are necessary as described in the invention. The resulting nanoparticles have excellent magnetic property for many applications.

WO 03/031323 A1

Synthesis of Mono-disperse and Highly-Crystalline Nano-particles of Metals, Alloys, Metal Oxides, and Multi-metallic Oxides without a Size-selection Process

Technical Field

The present invention relates to a method for synthesizing highly crystalline and monodisperse nanoparticles of metals, multi-metallic alloys, monometallic oxides and multi-metallic oxides without a size-selection process.

Background Art

The advent of uniform nanoparticles has made a significant impact on many different technological areas such as high density magnetic data storage elements, high density single-electron transistor devices and highly efficient laser beam sources. These nanometer-sized particles possess new and interesting electrical, magnetic and optical properties compared to the existing and widely known particles in the sizes larger than micrometer range.

The surface property of nanoparticle materials is very critical, because nanoparticles have high surface to volume ratio and high surface defect ratio in comparison with bulk materials. In addition, quantum confinement effect of nanoparticles, which have intermediate sizes between molecules and macroscopic bulk materials, has increased the scientific and technological interests. These nanoparticles find applications in nanodevices, nonlinear optical materials, catalysts, and data storage devices. In particular, in the era of information and multimedia, there are increasing demands for the development

of magnetic data storage devices with high density, high speed, low electrical power consumption, and ultra-low weight. Recently intensive research has been conducted for the development of magnetic storage devices using magnetic nanoparticles. As a result, the synthesis of monodisperse nanoparticles with controllable sizes has been intensively pursued. However the synthesis of monodisperse magnetic nanoparticles turned out to be very difficult because of strong electromagnetic interaction between nanoparticles. [Science, 267 (1995) 1338, Journal of Applied Physics, 61 (1987) 3323, IEEE Transactions on Magnetism, 27 (1991) 5184]

Maghemite(γ-Fe_2O_3), a ferrimagnetic iron oxide material, has been commonly used as magnetic storage media for commercial magnetic tape and hard disk device applications since 1937, and even today it is being used widely as an important magnetic material essentially for storage media. However, due to the fact that the size of the existing maghemite particles are in the range of micrometers and the minimum area required for a magnetic storage element is determined by the size of the magnetic particles, the density of the magnetic media is limited by the size of the magnetic particles.

Recently, intensive research has been conducted for synthesizing uniform nanometer-sized magnetic nanoparticles for their applications to high density magnetic data storage media. In the conventional magnetic data storage media, the minimum magnetic storage element, which is called a magnetic domain, is the minimum magnetic unit oriented along the applied magnetic field, and the conventional magnetic storage element is an aggregate

of many small crystals of magnetic materials. However, unlike the conventional magnetic data storage media, the nanoparticles with uniform size and shape, if used as magnetic storage media, increases the storage area density significantly, whereby a magnetic storage density of so-called multi-terabits/in^2 based on the prospect of one particle-on-one bit system can be achieved. There exist already various synthetic methods for producing uniform spherical magnetic nanoparticles. Some of the examples are "Thermal decomposition of organometallic precursors", [Journal of Physical Chemistry, 84 (1980) 1621], "Sonochemical decomposition of organometallic precursors", [Journal of American Chemical Society, 118 (1996) 11960], "High temperature reduction of metal salts", [Journal of Applied Physics, 85 (1999) 4325, also Korean Patent KR2000-0011546], and "Reduction of metal salts in reverse micelles", [Journal of Physical Chemistry B, 103 (1999) 1805].

In particular, "Method of short-burst of nucleation induced by rapid injection of precursors into a hot surfactant solution followed by aging", [Journal of American Chemical Society, 115 (1993) 8706], has been most widely used for synthesizing monodisperse nanoparticles. In other methods, rod-shaped magnetic nanoparticles were synthesized through the use of oriented growth of spherical nanoparticles, [Journal of American Chemical Society, 1222 (2000) 8581] and [Science 291 (2001) 2115].

However, the size of the nanoparticles produced using these synthetic methods is not uniform. In addition, compared to the nanoparticles of II-VI semiconductors and noble metals such as gold, silver, and platinum, relatively

very little research has been conducted for the synthesis of monodisperse nanoparticles of transition metals and oxides. Also, it is a well-known fact that synthesizing uniform nanoparticles in their size and shape is not an easy task.

Meanwhile, Alivisatos, et al. disclosed the synthesis of nanoparticles of transition metal oxides such as iron oxide[gamma-Fe_2O_3, maghemite], manganese oxide[Mn_3O_4] and copper oxide[Cu_2O] by thermally decomposing metal Cupferron[N-nitrosophenylhydroxylamine[$C_6H_5N(NO)O^-$] precursors at high temperature in the presence of surfactant. However, the resultant nanoparticles are irregular in size and their crystallinity is very poor, and therefore, it is very difficult to form superlattices for the applications to magnetic data storage media. In addition, very expensive metal Cupferron complex precursor is used [Journal of American Chemical Society, 121 (1999) 11595].

Therefore, the main objective of the present invention is to disclose a method of synthesizing nanoparticles that overcome the deficiencies aforementioned.

Detailed Description of the Invention

The present invention is to disclose synthetic methods of fabricating uniform nanoparticles of metals, alloys, monometallic oxides and multi-metallic oxides without a size-selection process, where said particles are generally spherically shaped and uniform in size and shape, and as a result said uniform nanoparticles have desired properties aforementioned. Such uniformity in size in diameter and of shape allows the nanoparticles to form superlattices by self-

assembly, thereby said nanoparticles synthesized according to the present invention have a property of forming superlattices and said nanoparticles can be used as a high density magnetic data storage media as high as in the range of terabits/in^2.

Another object of the present invention is to disclose a synthetic method of fabricating nanoparticles of metals, alloys, mono-metallic oxides and multi-metallic oxides with the characteristics, where the nanoparticles can be dispersed many times in various solvents without being aggregated, and the nanoparticles maintain the same particle size and also they do not aggregate even when said nanoparticles are recovered in a powder form.

Such physical properties of non-aggregation and maintaining the same particle size when said nanoparticles are recovered according to the present invention expand the possibility of applications area and the usability of said nanoparticles and also suggest an improved possibility of recycling and reusing.

Another object of the present invention is to disclose methods of synthesizing highly crystalline and monodisperse spherical metal particles by high temperature decomposition and aging of metal surfactant complex produced by reacting a precursor and a surfactant. The object of the present invention is to further disclose methods of synthesizing metal oxide nanoparticles uniform in size and shape by a controlled oxidation process of the resultant metal nanoparticles by using an oxidant. Said monodisperse nanoparticles synthesized according to the present invention as described previously induce the formation of superlattices through a self-assembly

process, and as a result said monodisperse nanoparticle superlattices can be used as a high density magnetic data storage media

The synthetic method of fabricating nanoparticles of metals and metal oxides is described in reference to Figs. 1 through 3 in the following.

Fig. 1 is a flowchart showing the process of synthesizing nanoparticles of metals and metal oxides according to the present invention. Fig. 2 is a flowchart showing the process of directly synthesizing metal oxide nanoparticles without going through the process of synthesizing metal nanoparticles first according to the present invention. Fig. 3 is a flowchart showing the process of synthesizing larger nanoparticles by growing the nanoparticles already produced according to the present invention.

According to the present invention and in reference to Fig. 1, nanoparticles of metals and metal oxides can be synthesized by following three steps described below. Step A 101, 102: After preparing a metal precursor and a suitable surfactant in a solvent, a metal surfactant complex is synthesized by a process of reaction of a metal precursor and a surfactant. Step B 103: Monodisperse metal nanoparticles are produced by decomposing the metal surfactant complex. Step C 104: Completion of the formation of said synthesized metal nanoparticles by adding a poor solvent followed by centrifuging. Furthermore, the following additional step, Step D 105, 106, is followed in order to synthetically produce nanoparticles of metal oxides. Step D 105, 106: After dispersing metal nanoparticles, said nanoparticles are oxidized

using an oxidant to produce metal oxide nanoparticles, and then the metal oxide nanoparticles are obtained.

According to another aspect of the present invention and referring to Fig. 2, metal oxide nanoparticles can be synthesized directly by rapidly injecting a metal precursor into a solution containing both surfactant and oxidant followed by thermal decomposition, and then finally by a process of obtaining desired metal oxide nanoparticles.

According to yet another aspect of the present invention, larger nanoparticles in size in the range of about 12nm to 50nm can be synthesized. Referring to Fig. 3, after synthesizing smaller nanoparticles in size in the range of about 4nm to 11nm following the procedures described in reference to Figs. 1 and 2 above, a metal-surfactant complex is added to the previously prepared nanoparticles of size in the range from about 4nm to 11nm followed by a thermal decomposition process to obtain larger size nanoparticles ranging from about 12nm to 50nm.

Normally, all the reaction processes described above in reference to Figs. 1 through 3, may be carried out under an inert gas environment in a glove box filled with an inert gas such as nitrogen or argon, or the Schrenk technique can be utilized.

More specifically, in reference to Fig.1 and in Step A 101, 102 in synthesizing metal nanoparticles, metallic precursors are injected into a surfactant solution at a temperature ranging from 30°C to 200°C for producing metal-surfactant complexes. In Step B 103, the synthesized metal surfactant

complex is thermally decomposed by refluxing at a temperature ranging from 30°C to 500°C in order to obtain metal nanoparticles.

According to the present invention, following metal precursors can be used for producing the desired nanoparticles; various organometallic compounds including typically iron pentacarbonyl [$Fe(CO)_5$], ferrocene, cobalt tricarbonylnitrosyl [$Co(CO)_3(NO)$], cyclopentadienylcobalt-tricarbonyl [$Co(CO)_3(C_5H_5)$)], dicobalt octacarbonyl[$Co_2(CO)_8$], chromium hexacarbonyl [$Cr(CO)_6$], Nickel tetracarbonyl [$Ni(CO)_4$], dimanganese decacarbonyl [$Mn_2(CO)_{10}$], metal acetylacetonate compounds including typically iron acetylacetonate [$Fe(acac)_3$], cobalt acetylacetonate[$Co(acac)_3$], barium acetylacetonate[$Ba(acac)_2$], strontium acetylacetonate[$Sr(acac)_2$], platinum acetylacetonate[$Pt(acac)_2$], palladium acetylacetonate[$Pd(acac)_2$], and metal alkoxide compounds including typically titanium tetraisopropoxide [$Ti(^iOC_3H_7)_4$], zirconium tetrabutoxide [$Zr(OC_4H_9)_4$].

More broadly, the metals used in the precursors according to the present invention include typically iron[Fe], cobalt[Co], nickel[Ni], chromium[Cr], manganese[Mn], barium[Ba], strontium[Sr], titanium[Ti], zirconium[Zr], platinum [Pt], palladium[Pd], and the groups II through X transition metals in particular. The ligands include typically carbonyl[CO], nitrosyl[NO], cyclopentadienyl[C_5H_5], acetate, aromatic compounds and alkoxide family. The following metal salts can also be used as precursors. These metal salts include typically iron(III) chloride[$FeCl_3$], iron(II) chloride[$FeCl_2$], iron(II) sulfate[$FeSO_4$], iron(III) nitrate[$Fe(NO_3)_3$], cobalt(III) chloride[$CoCl_3$], cobalt(II) chloride[$CoCl_2$], cobalt(III)

nitrate[$Co(NO_3)_3$], nickel(II) sulfate[$NiSO_4$], nickel(II) chloride[$NiCl_2$], nickel(II) nitrate[$Ni(NO_3)_2$], titanium tetrachloride[$TiCl_4$], zirconium tetrachloride[$ZrCl_4$], hydrogen hexachloroplatinate(IV)[H_2PtCl_6], hydrogen hexachloropalladiate(IV) [H_2PdCl_6], barium chloride[$BaCl_2$], barium sulfate[$BaSO_4$], strontium chloride[$SrCl_2$] and strontium sulfate[$SrSO_4$]. These metal salts consist of various metals including typically iron[Fe], cobalt[Co], nickel[Ni], chromium[Cr], manganese[Mn], barium [Ba], strontium[Sr], titanium[Ti], zirconium[Zr], platinum[Pt], palladium[Pd], and anions including typically chloride[Cl^-], nitrate[NO_3^-], sulfate[SO_4^{2-}], phosphate [PO_4^{3-}] and alkoxides. Furthermore, in synthesizing nanoparticles of alloys and multi-metallic oxides, mixtures of two or more metal precursors mentioned above can be used as precursors according to the present invention.

According to the present invention, referring to Fig, 1, in Step A 101, 102, following surfactants can be used for stabilizing the nanoparticles including cationic surfactants including typically alkyltrimethylammonium halides such as cetyltrimethylammonium bromide, neutral surfactants including typically oleic acid, trioctylphosphine oxide(TOPO) and triphenylphosphine(TOP), alkyl amines such as oleylamine, trioctylamine, octylamine and alkyl thiols, and anionic surfactants including typically sodium alkyl sulfates and sodium alkyl phosphates. Mixtures of two or more surfactants can be used as described in some cases.

The oxidants used in the present invention include typically amine N-oxide such as pyridine N-oxide and trimethylamine N-oxide, and also hydrogen

peroxide and oxygen.

The solvents used in the present invention should have high enough boiling temperature because the metal-surfactant precursors must be decomposed to produce metal nanoparticles. Such solvents include typically ethers such as octyl ether, butyl ether, hexyl ether and decyl ether, heterocyclic compounds such as pyridine and tetrahydrofurane(THF), and also aromatic compounds such as toluene, xylene, mesitylene, benzene, and dimethyl sulfoxide(DMSO), and dimethylformamide(DMF), and alcohols such as octyl alcohol, and decanol, and hydrocarbons such as pentane, hexane, heptane, octane, decane, dodecane, tetradecane, hexadecane, and also water. Again, in order to thermally decompose a metal surfactant complex for synthesizing desired nanoparticles according to the present invention, the solvent to be used should have preferably high boiling temperature close to the thermal decomposition temperature of said metal surfactant complex.

According to the present invention, metal nanoparticles can be synthesized by controlled decomposition of a metal surfactant complex, and also metal oxide nanoparticles can be synthesized by a further process of oxidation of the resulting metal nanoparticles obtained through the previous synthesis step. The size and shape of said nanoparticles can be controlled by varying the synthesis parameters such as primarily the volume of a surfactant, reaction temperature and reaction time. For example, referring to Fig. 1, the particle size in diameter of the metal nanoparticles synthesized in Step B 103 is

uniform and this uniformity in size is preserved when metal oxide nanoparticles are synthesized in Step D 105, 106 meaning that the size of the metal oxide nanoparticles does not change when the metal nanoparticles are synthesized according to the present invention. Furthermore, the size of nanoparticles can be easily controlled from 2nm to as large as 50nm by varying the concentration of the surfactant with respect to the solvent used, meaning that monodisperse nanoparticles of metals and metal oxides can be synthesized and the size of the nanoparticles can be easily controlled according to the present invention. When the size of nanoparticles is controlled by varying the volume of the surfactant used, it was confirmed experimentally that the diameter of the metal nanoparticles is increased in proportion to the volume of the surfactant used in Step A 101, 102. Therefore, metal and metal oxide of nanoparticles in various sizes can be synthesized by controlling the ratio of metallic precursor to surfactant within a wide range according to the present invention, wherein the applicable molar ratio of metallic precursor to surfactant ranges from 1: 0.1 to 1: 100, and preferably from 1: 0.1 to 1: 20. Furthermore, it was also experimentally confirmed that the size of the metal nanoparticles became smaller as the thermal decomposition temperature was lowered as well as the reaction time was shortened.

According to the present invention, as described previously, a metal surfactant complex is synthesized first by reacting a metal precursor and a surfactant, where the reaction of a metal precursor and a surfactant can be performed at room temperature or lower than room temperature depending

upon the types of the metal precursors and surfactants used, but generally a low level of heating is necessary. During the process of synthesizing a metal surfactant complex, the reaction temperature is maintained preferably in the range from 30°C to 200°C.

According to the present invention, monodisperse metal nanoparticles with uniform size and shape are formed when a metal surfactant complex is thermally decomposed under an appropriate reaction condition, where the temperature of the thermal decomposition of the metal surfactant complex varies somewhat depending upon the type of the metal surfactant complex used. Also, in order to thermally decompose the metal surfactant complex, preferably, the complex is heated to a temperature in the range of 50°C to 500°C and such temperature level is maintained in order to carry out the thermal decomposition of the metal surfactant complex according to the present invention.

Furthermore, according to the present invention, in order to synthesize metal oxide nanoparticles, the amount of the oxidant needed for oxidizing the metal nanoparticles is determined in such a way that the amount is sufficient enough to oxidize all the metal nanoparticles desired, where the molar ratio of the nanoparticles and the oxidant ranges, in general, from 1: 0.1 to 1: 100, and preferably in the range from 1: 0.1 to 1: 20.

In the following, referring to Fig. 2, a procedure of synthesizing metal oxide nanoparticles by reacting a metal precursor, a surfactant and an oxidant according to the present invention 201, 202, 203. Specifically, a metal

precursor, a surfactant and an oxidant are mixed at low temperature, for example, in the range from −100°C to 200°C, and preferably at the level of temperature about 100°C. The resulting mixture is then heated to a level of temperature ranging from 30°C and 500°C and preferably at the level of temperature about 300°C in order to complete the process of synthesizing metal oxide nanoparticles. During this heating period the heating rate is controlled preferably within the range between 1°C/min. to 20°C/min. depending upon the desired property of the nanoparticles according to the present invention.

Furthermore, referring to Fig. 3, nanoparticles larger in size ranging from 12nm to 50nm can be synthesized, as described previously, by thermally decomposing the mixture of previously synthesized nanoparticles in the size normally less than 11nm and a metal surfactant complex with a molar rate ranging from 1: 0.1 to 1: 100 according to the present invention 301, 302, 303, 304.

According to the present invention, sufficient reaction time in each processing step is given in order to complete each step of synthesis generally ranging from 1 minute to 24 hours. In addition, the desired nanoparticles of metals and metal oxides can be separated and retrieved by contrifugation of the reaction mixture or the precipitation by adding a poor solvent according to the present invention as described previously, where the poor solvent is a solvent that can not disperse nanoparticles effectively and induce the precipitation of the nanoparticles.

The nanoparticles with particle size ranging from 2nm to 50nm,

synthesized according to the present invention, form superlattices due primarily to the characteristics of uniformity in size and shape that the nanoparticles possess according to the present invention, thereby such nanoparticles exhibit a good magnetic property. In particular, the magnetic nanoparticles bigger than 16nm in diameter exhibit the property of ferromagnetism or ferrimagnetism with high magnetic moment sufficient to be used as magnetic data storage elements, and furthermore, the nanoparticles as large as 50nm synthesized using the procedure described above, according to the present invention, have potentially many uses in industrial applications.

In general, nanostructured magnetic materials exhibit different temperature-dependent magnetic characteristics such as ferromagnetism at low temperature or superparamagnetism at high temperature. The reversible transition temperature between ferromagnetism and superparamagnetism is called blocking temperature (T_b). The blocking temperature should be high, because the materials should exhibit ferromagnetism or ferrimagnetism for suitable applications to magnetic data storage media.

Brief Description of the Drawings

Fig. 1 is a schematic flow chart showing a synthetic procedure of nanoparticles of metals and metal oxides according to the present invention.

Fig. 2 is a schematic flow chart showing a direct synthetic procedure of

metal oxide nanoparticles without going through a synthesis process of metal nanoparticles according to the present invention.

Fig. 3 is a schematic flow chart showing a synthetic procedure of larger nanoparticles by growing the nanoparticles.

Fig. 4 is an exemplary TEM image of the spherical iron nanoparticles of 11nm in diameter synthesized according to Embodiment 1.

Fig. 5 is an exemplary TEM image of a 2-dimensional array of the spherical iron oxide nanoparticles of 11nm in diameter synthesized according to Embodiment 2.

Fig. 6 is an exemplary. TEM image of a 3-dimensional array of the spherical iron oxide nanoparticles of 11nm in diameter synthesized according to Embodiment 2.

Fig. 7 is an exemplary high resolution TEM image of spherical iron oxide nanoparticles of 11nm in diameter synthesized according to Embodiment 2.

Fig. 8 is an exemplary TEM image of the spherical iron oxide nanoparticles of 7nm in diameter synthesized according to Embodiment 3.

Fig. 9 is an exemplary TEM image of the spherical iron oxide nanoparticles of 4nm in diameter synthesized according to Embodiment 4.

Fig. 10 is an exemplary TEM image of the spherical iron oxide nanoparticles of 16nm in diameter synthesized according to Embodiment 5.

Fig. 11 is an exemplary TEM image of a 2-dimensional array of the spherical iron oxide nanoparticles of 13nm in diameter synthesized according to

Embodiment 6.

Fig. 12 is an exemplary TEM image of a 2-dimensional array of the spherical cobalt-iron alloy nanoparticles of 6nm in diameter synthesized according to Embodiment 7.

Fig. 13 is an exemplary TEM image of a 2-dimensional array of the spherical cobalt ferrite ($CoFe_2O_4$) nanoparticles of 9nm in diameter synthesized according to Embodiment 8.

Fig. 14 is an exemplary TEM image of a 2-dimensional array of the spherical cobalt ferrite ($CoFe_2O_4$) nanoparticles of 6nm in diameter synthesized according to Embodiment 9.

Fig. 15 is an exemplary TEM image of a 3-dimensional array of the spherical cobalt ferrite ($CoFe_2O_4$) nanoparticles of 6nm in diameter synthesized according to Embodiment 9.

Fig. 16 is an exemplary TEM image of a 2-dimensional array of the spherically shaped cobalt ferrite ($CoFe_2O_4$) nanoparticles of 8nm synthesized according to Embodiment 10.

Fig. 17 is a graph showing the relationships of magnetization versus temperature for the spherical iron oxide nanoparticles in three different sizes of 4nm, 13nm and 16nm in diameter synthesized according to the Embodiments 4, 5, and 6, respectively.

Best Modes for Carrying Out the Invention

As aforementioned, spherically shaped metal oxide nanoparticles can

be synthesized according to the present invention, where such nanoparticles exhibit an excellent magnetic property for magnetic data storage media applications, and such property can be demonstrated by measuring the blocking temperatures of various sizes of metal oxide nanoparticles according to the present invention.

The procedures and results of the best modes of carrying out the present invention are described in the following. However, the procedures and results presented here are merely illustrative examples of carrying out the implementation of the underlying ideas and procedures of the present invention, and the presentation of the exemplary embodiments given in the following is neither intended for exhaustively illustrating the basic ideas and procedures nor limiting the scope of the present invention. Furthermore, those who are familiar with the art should be able to easily derive variations and modifications of the underlying ideas and procedures of the present invention.

Embodiment 1: Synthesis of monodisperse and spherically shaped iron nanoparticles

As a first exemplary embodiment of synthesizing monodisperse and spherically shaped iron nanoparticles according to the present invention disclosed here, 0.2mL of iron pentacarbonyl [$Fe(CO)_5$] was added to a mixture containing 10mL of dehydrated octyl ether and 1.25g of oleic acid under inert atmosphere, and heated the resulting mixture at 110°C to obtain an iron-oleic acid complex, where the resulting reactant mixture was heated to reflux and

was aged for 1 hour at the reflux temperature. During this process, the iron pentacarbonyl [$Fe(CO)_5$] was thermally decomposed completely, and iron atoms were generated. The resulting solution was cooled to room temperature, and ethanol was added to yield a black precipitate, which was then separated by centrifuging. The resulting supernatant was discarded. After repeating this washing process at least three times, the ethanol contained in the remainder was removed by vacuum drying. The resulting product was redispersed easily in hexane to form desired iron nanoparticles. The measured diameter of the resulting nanoparticles The TEM(Transmission Electron Microscope) image of the resulting product, iron nanoparticles, synthesized by the methods presented here according to the present invention is shown in Fig. 4, which is an exemplary TEM image of the 11 nm spherical iron nanoparticles of 11nm in diameter synthesized according to Embodiment 1, which image indicates that the resulting nanoparticles are spherically shaped and uniform, and also they appear to be monodisperse.

Embodiment 2: Synthesis of monodisperse and spherically shaped iron oxide nanoparticles-1

In order to synthesize monodisperse and spherically shaped iron oxide nanoparticles of 7nm in diameter according to the present invention, similarly to the procedure described in Embodiment 1 above, 0.2mL of iron pentacarbonyl [$Fe(CO)_5$] was added to a mixture containing 10mL of dehydrated octyl ether and 1.25g of oleic acid under an inert atmosphere and the resulting mixture is

heated at 110°C to form an iron-oleic acid complex. The resulting reactant mixture was heated to reflux and aged for 1 hour at the reflux temperature. During this process, iron pentacarbonyl [$Fe(CO)_5$] was thermally decomposed completely and iron atoms were generated. In order to obtain monodisperse and spherically shaped iron oxide(maghemite, γ-Fe_2O_3) nanoparticles, the resulting red colored solution was cooled to room temperature. Then, 0.36g of trimethylamine N-oxide, an oxidant, was added, and the resulting black colored mixture was again heated to 300°C and maintained at this temperature for 30 minutes, and as a result, a brown solution was formed. This color change from red to brown observed visually indicating that an iron oxide was formed. The oxide solution was cooled to room temperature. To remove excess surfactant and the by-product, anhydrous- highly degassed ethanol was added to wash, yielding a black precipitate. The supernatant was separated and discarded by either decantation or centrifugation. After this washing process was repeated at least three times, the ethanol was removed by vacuum drying. The resulting product was easily redispersed in hexane. The TEM images of the resulting products of iron nanoparticles synthesized according to this procedure, are shown in Figs. 5 through 7, where an exemplary TEM image of a 2-dimensional array of the spherical iron oxide nanoparticles of 11nm in diameter synthesized according to the present invention is shown in Fig.5, and an exemplary TEM image of a 3-dimensional array of the spherical iron oxide nanoparticles of 11nm in diameter synthesized according to the present invention is shown in Fig. 6., and also an exemplary high resolution TEM image

of the spherical iron oxide nanoparticles of 11nm in diameter synthesized according to the present invention presented in this Embodiment 2 is shown in Fig. 7, respectively. The TEM images in Figs. 5 through 7 illustrate that the spherical iron oxide nanoparticles of 11nm in diameter synthesized according to the present invention presented in Embodiment 2 are monodisperse.

Embodiment 3: Synthesis of monodisperse spherical iron oxide nanoparticles-2

Monodisperse spherical metal oxide nanoparticles of 7nm in diameter were synthesized using the same reaction conditions described in Embodiment 2, except that the amount of the surfactant used is reduced to 0.85g. An exemplary TEM image of the 7nm spherical iron oxide nanoparticles synthesized according to the present invention is as shown in Fig. 8, indicating that the 7nm spherical iron oxide nanoparticles are monodisperse.

Embodiment 4: Synthesis of monodisperse spherical iron oxide nanoparticles-3

Monodisperse spherical metal oxide nanoparticles of 4nm in diameter were synthesized using the same reaction conditions described in Embodiment 2, except that the amount of the surfactant used is reduced to 0.43g. An exemplary TEM image of the 4nm spherical iron oxide nanoparticles synthesized according to the present invention is as shown in Fig. 9, indicating that the 4nm spherical iron oxide nanoparticles are monodisperse.

Embodiment 5: Synthesis of monodisperse spherical iron oxide nanoparticles-4

Monodisperse spherical metal oxide nanoparticles of 16nm in diameter were synthesized using the same reaction conditions described in Embodiment 2, except that the amount of the surfactant used is increased to 1.72g. An exemplary TEM image of the 16nm spherical iron oxide nanoparticles synthesized according to present invention is shown in Fig. 10, indicating that the 16 nm spherical iron oxide nanoparticles are monodisperse.

Embodiment 6: Direct synthesis of monodisperse spherical iron oxide nanoparticles-5

0.2 mL of iron pentacarbonyl ($Fe(CO)_5$) was injected into a solution containing 7 mL of dehydrated octyl ether, 0.91g of lauric acid, and 0.57g of trimethylamine N-oxide at 100 in inert atmosphere. As soon as iron pentacarbonyl ($Fe(CO)_5$) was injected into the mixture, the temperature rose to 120°C and iron oxide nuclei were generated. This solution was heated to 300°C and kept it for 1 hour. During this process, iron pentacarbonyl ($Fe(CO)_5$) was thermally decomposed completely. At this time the initial black solution was turned into red and the solution color gradually became brown as the temperature was increased, indicating visually that iron oxide was formed. To remove excess surfactant and by-product, anhydrous and degassed ethanol was added to yield a black precipitate. The supernatant was discarded either by

decantation or by centrifugation. After this washing process was repeated three times or more, ethanol was removed by vacuum drying. The resulting product was easily redispersed in hexane. The TEM image of the resulting product synthesized according to Embodiment 6 is presented in Fig. 11. Fig. 11 is an example of the TEM image of a 2-dimensional array of 13 nm spherical iron oxide nanoparticles synthesized according to Embodiment 6. The TEM image of Fig. 11 reveals that the 13nm spherical iron oxide nanoparticles are monodisperse.

Embodiment 7: Synthesis of spherical iron-cobalt alloy nanoparticles

0.3mL of iron pentacarbonyl ($Fe(CO)_5$) and 0.15mL of cyclopentadienylcobalt tricarbonyl ($Co(CO)_3(C_5H_5)$) were added to a mixture containing 10 mL of dehydrated octyl ether and 0.9g of oleic acid under an inert atmosphere and heated at 110 °C, which generated the mixture of iron-oleic acid and cobalt-oleic acid complexe. The resulting reaction mixture was heated to 300°C and aged for 1 hour at this temperature. During this process, an organometallic precursor was thermally decomposed completely and metal alloy nanoparticles were formed. In order to obtain monodisperse spherical iron-cobalt alloy nanoparticles, anhydrous and degassed ethanol was added to yield a black precipitate. The supernatant was discarded either by decantation or by centrifugation. After this washing process was repeated at least three times, ethanol was removed by vacuum drying. The resulting product was easily redispersed in hexane. A TEM image of the resulting product synthesized

according to Embodiment 7 is shown in Fig. 12. Fig. 12 is an example of a TEM image of a 2-dimensional array of 6 nm spherical cobalt-iron alloy nanoparticles synthesized according to Embodiment 7. The TEM image of Fig. 12 indicates that the 6nm spherical iron-cobalt alloy nanoparticles are monodisperse.

Embodiment 8: Synthesis of monodisperse spherical cobalt ferrite ($CoFe_2O_4$) nanoparticles-1

0.3mL of iron pentacarbonyl ($Fe(CO)_5$) and 0.15mL of cyclopentadienylcobalt tricarbonyl ($Co(CO)_3(C_5H_5)$) were added to a mixture containing 10mL of dehydrated octyl ether and 1.95g of oleic acid under inert atmosphere and heated at 110°C. The resulting mixture was heated to 300°C and kept for 30minutes at this temperature. During this process, the organometallic precursors were thermally decomposed completely and metal alloy nanoparticles were formed. In order to obtain the monodisperse spherical cobalt ferrite nanoparticles, the solution was cooled to room temperature, and 0.38g of trimethylamine N-oxide was added. The mixture was then heated to 300°C and maintained at this temperature for 30min, whereupon it formed a brown solution and this color change from red to brown indicated visually the cobalt ferrite was formed. And then the solution was cooled to room temperature again. To remove excess surfactant and by-product, anhydrous and degassed ethanol was added to yield a black precipitate. The supernatant

was discarded either by decanting or by centrifugation. After this washing process was repeated three times or more, ethanol was removed by vacuum drying. The resulting products were easily redispersed in hexane. The TEM image of metal oxide nanoparticles synthesized according to this procedure is shown in Fig. 13. Fig. 13 is an example of a TEM image of a 2-dimensional array of 9nm spherical cobalt ferrite ($CoFe_2O_4$) nanoparticles synthesized according to Embodiment 8. The TEM image of Fig. 13 indicates that the 9nm spherical cobalt ferrite ($CoFe_2O_4$) nanoparticles are monodisperse.

Embodiment 9: Synthesis of monodisperse spherical cobalt ferrite ($CoFe_2O_4$) nanoparticles-2

Monodisperse spherical cobalt ferrite ($CoFe_2O_4$) nanoparticles were synthesized using the same reaction conditions with Embodiment 8, except that the amount of the surfactant used is reduced to 0.9g. The TEM images of nanoparticles synthesized according to this procedure are shown in Figs. 14 and 15. Fig. 14 is an example of TEM image of a 2-dimensional array of 6 nm spherical cobalt ferrite ($CoFe_2O_4$) nanoparticles synthesized according to Embodiment 9, and Fig. 15 is an example of TEM image of a 3-dimensional array of 6 nm spherical cobalt ferrite ($CoFe_2O_4$) nanoparticles synthesized according to Embodiment 9. The TEM images of Figs. 14 and 15 indicate that the 6nm spherical cobalt ferrite ($CoFe_2O_4$) nanoparticles are monodisperse.

Embodiment 10: Synthesis of monodisperse spherical cobalt ferrite ($CoFe_2O_4$)

nanoparticles-3

Monodisperse spherical cobalt ferrite ($CoFe_2O_4$) nanoparticles were synthesized using the same reaction conditions with Embodiment 8, except that the amount of the surfactant used is reduced to 1.2g. A TEM image of nanoparticles synthesized according to this procedure is shown in Fig. 16. Fig. 16 is an example of TEM image of a 2-dimensional array of 8 nm spherical cobalt ferrite ($CoFe_2O_4$) nanoparticles synthesized according to Embodiment 10. The TEM image of Fig. 16 indicates that the 8 nm spherical cobalt ferrite ($CoFe_2O_4$) nanoparticles are monodisperse.

Embodiment 11: Magnetic property of spherical iron oxide nanoparticles

The magnetic property was tested on the 4, 13, and 16 nm sized spherical iron oxide nanoparticles synthesized according to Embodiments 4, 5 and 6 by using a superconducting quantum interference device (SQUID). The temperature dependence of the magnetization was measured using zero-field cooling (ZFC) and field cooling (FC) procedures in an applied magnetic field of 100 One between 5 and 300 K. The resulting plot of temperature versus magnetization with ZFC is shown in Fig. 17. Fig. 17 is a graph of magnetization versus temperature curves for 4, 13, and 16 nm spherical iron oxide nanoparticles synthesized using the methods in Embodiments 4, 5, and 6, respectively. The graph of Fig. 17 indicates that the blocking temperatures of the spherical iron oxide nanoparticles with particle diameters of 4, 13 and 16nm were found to be 25, 200, and 290°K, respectively. In particular, because

nanoparticles with the diameter of over 16nm are ferrimagnetic, they can be used for magnetic data storage devices.

Industrial Applicability

The monodisperse and highly crystalline nanoparticles of metals, alloys and metal oxides synthesized according to the present invention display very unique and good and consistent electrical, magnetic as well as optical properties. Particularly, their magnetic property due to excellent uniformity in size of the metal, alloy and metal oxide nanoparticles is attractive for using such nanoparticles as high density magnetic storage media such as hard disks and magnetic tapes, and also such monodisperse and highly crystalline nanoparticles are potentially useful for forming ultra-small single-electron transistor devices and for highly efficient laser light sources.

What is claimed is:

1. A method for producing metal or metal alloy nanoparticles, comprising the steps of;

forming a metal-surfactant complex by reacting a metal precursor and a surfactant in a solvent,

synthesizing monodisperse metal nanoparticles by thermally decomposing said metal-surfactant complex, and

completing formation of said synthesized metal or metal alloy nanoparticles by adding a poor solvent followed by centrifuging.

2. The method of claim 1, in order to produce highly crystalline monodisperse metal oxide nanoparticles, further comprising the steps of;

synthesizing said metal oxide nanoparticles by treating said synthesized nanoparticles with an oxidant for a controlled oxidation process, and

completing the formation of synthesized metal oxide nanoparticles by adding a poor solvent followed by centrifuging.

3. The method of claim 1 or 2, wherein said metallic precursors include typically Fe, Co, Ni, Cr, Mn, Ba, Sr, Ti, Zr, Pt, Pd, and metallic compound ligands including typically –CO, -NO, $-C_5H_5$ and alkoxides

4. The methods of claim 1 or 2, wherein metallic precursors include typically iron pentacarbonyl $[Fe(CO)_5]$, ferrocene, cobalt

tricarbonylnitrosyl[$Co(CO)_3(NO)$], cyclopentadienylcobalt-tricarbonyl[$Co(CO)_3(C_5H_5)$], dicobalt octacarbonyl [$Co_2(CO)_8$], chromium hexacarbonyl[$Cr(CO)_6$], nickel tetracarbonyl[$Ni(CO)_4$], dimanganese decacarbonyl[$Mn_2(CO)_{10}$], iron acetylacetonate[$Fe(acac)_3$], cobalt acetylacetonate[Co(acac)3], barium acetylacetonate[$Ba(acac)_2$], strontium acetylacetonate[$Sr(acac)_2$], platinum acetylacetonate[$Pt(acac)_2$], palladium acetylacetonate[$Pd(acac)_2$], titanium tetraisopropoxide[$Ti(^iOC_3H_7)_4$], zirconium tetrabutoxide[$Zr(OC_4H_9)_4$], iron(III) chloride[$FeCl_3$], iron(II) chloride[$FeCl_2$], iron(II) sulfate[$FeSO_4$], iron(III) nitrate[$Fe(NO_3)_3$], cobalt(III) chloride[$CoCl_3$], cobalt(II) chloride[$CoCl_2$], cobalt(III) nitrate[$Co(NO_3)_3$], nickel(II) sulfate[$NiSO_4$], nickel(II) chloride[$NiCl_2$], nickel(II) nitrate[$Ni(NO_3)_2$], titanium tetrachloride[$TiCl_4$], zirconium tetrachloride[$ZrCl_4$], hydrogen hexachloroplatinate(IV)[H_2PtCl_6], hydrogen hexachloropalladiate(IV)[H_2PdCl_6], barium chloride[$BaCl_2$], barium sulfate[$BaSO_4$], strontium chloride[$SrCl_2$], strontium sulfate[$SrSO_4$]

5. The methods of claim 1 or 2, wherein said surfactants include cationic surfactants including typically alkyltrimethylammonium halide system such as cetyltrimethylammonium bromide, neutral surfactants including typically oleic acid, trioctylphosphine oxide (TOPO), triphenylphosphine (TOP), alkyl amine such as oleylamine, trioctylamine, octylamine, alkylthiol, and anionic surfactants including typically sodium alkylsulfate and sodium alkylphosphate.

6. The methods of claim 1 or 2, wherein solvents include typically

ether compounds such as octyl ether, butyl ether, hexyl ether, decyl ether, heterocyclic compounds such as pyridine, tetrahydrofurane(THF), aromatic compounds such as toluene, xylene, mesitylene, benzene, and dimethyl sulfoxide (DMSO), and dimethylformamide (DMF), and alcohols such as octylalcohol, decanol, and hydrocarbons such as pentane, hexane, heptane, octane, decane, dodecane, tetradecane, hexadecane, and water.

7. The method of claim 2, wherein oxidants include typically amine N-oxide such as pyridine N-oxide, trimethylamine N-oxide, and hydrogen peroxide, and also oxygen.

8. The method of claim 1, wherein above metallic precursors were injected into a solution containing above surfactants at 30°C to 200 °C in Step (A), the formation step of metal-surfactant complex.

9. The method of claim 1, wherein said metal-surfactant complex is decomposed at 50°C to 500°C in the step of forming said monodisperse metal nanoparticles.

10. The method of claim 1, wherein said metal nanoparticles are precipitated from said dispersed solution by adding a poor solvent followed by centrifugation process to obtain said metal nanoparticles in a powder form.

11. The method of claim 2, said metal nanoparticles is dispersed in said solvent, and said oxidant is added at a temperature between –100°C to 200 °C, the resulting mixed solution is heat-treated at a temperature ranging from 30°C to 500°C for a duration ranging from 1 minute to 24 hours continuously to synthesize said metal oxide nanoparticles.

12. The method of claim 1, wherein the molar ratio of said metallic precursor to said surfactant ranges from 1 : 0.1 to 1 : 100 is maintained.

13. The method of claim 2, wherein the molar ratio of said metal nanoparticles to said oxidant ranges from 1 : 0.1 to 1 : 100 is maintained.

14. The method of claim 9, wherein the heating rate for reaching said decomposition temperature is in the range of 1°C/min. to 20°C/min.

15. The method of claim 11, wherein the heating rate for reaching said oxidation temperature is in the range of 1°C/min. to 20°C/min.

16. The method of direct synthesis of metal oxide nanoparticles, comprising the steps of;

synthesizing monodisperse metal oxide nanoparticles by adding said metal precursor, said oxidant, and said surfactant to said solvent in one container to prepare a mixed solution followed by a heating process, and

completing the formation of said metal oxide nanoparticles by adding a poor solvent followed by a centrifugation process.

17. The method of claim 16, wherein said mixed solution is heat-treated at a temperature in the range of 30°C to 500 °C for a duration from 1 minute to 24 hours continuously to synthesize said metal oxide nanoparticles.

18. The methods of claim 1, claim 2 or claim 16, in order to increase the size of said nanoparticles smaller than 11nm, further comprising a step of;

heat-treating a mixed solution of said metal surfactant complex and said nanoparticles of size smaller than 11nm, where the molar ratio of said metal nanoparticles and said metal surfactant complex is in the range of 1 : 0.1 to 1 : 100.

19. The methods of claim 1, claim 2 or claim 16, wherein the resulting metal or metal oxide nanoparticles form a supperlattice by self assembly and produce a magnetic storage media with very high area density.

FIG. 1

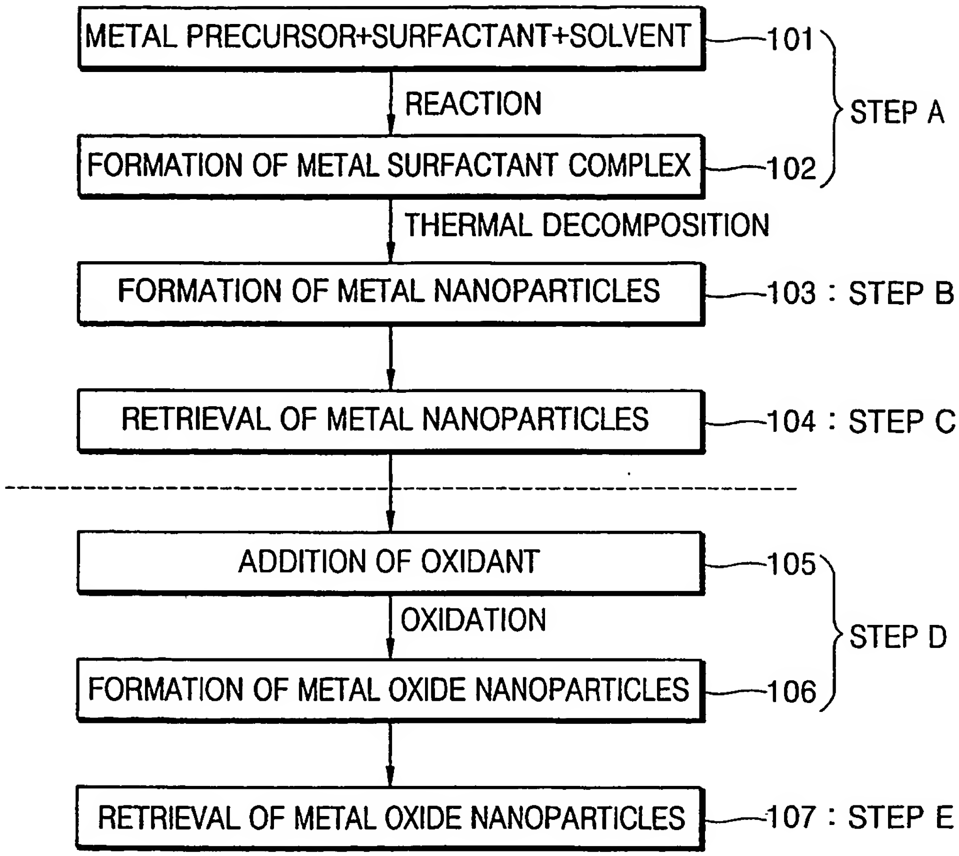

METAL PRECURSOR+SURFACTANT+SOLVENT
101
REACTION
FORMATION OF METAL SURFACTANT COMPLEX
102
STEP A
THERMAL DECOMPOSITION
FORMATION OF METAL NANOPARTICLES
103 : STEP B
RETRIEVAL OF METAL NANOPARTICLES
104 : STEP C
ADDITION OF OXIDANT
105
OXIDATION
FORMATION OF METAL OXIDE NANOPARTICLES
106
STEP D
RETRIEVAL OF METAL OXIDE NANOPARTICLES
107 : STEP E

FIG. 2

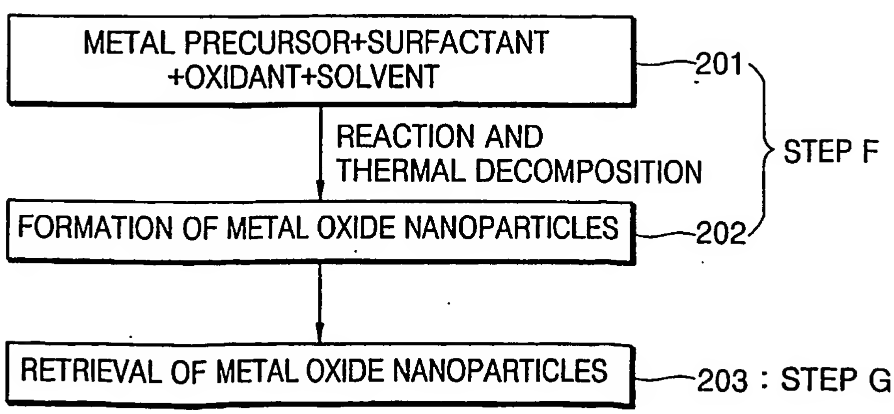

METAL PRECURSOR+SURFACTANT
+OXIDANT+SOLVENT
201
REACTION AND
THERMAL DECOMPOSITION
FORMATION OF METAL OXIDE NANOPARTICLES
202
STEP F
RETRIEVAL OF METAL OXIDE NANOPARTICLES
203 : STEP G

FIG. 3

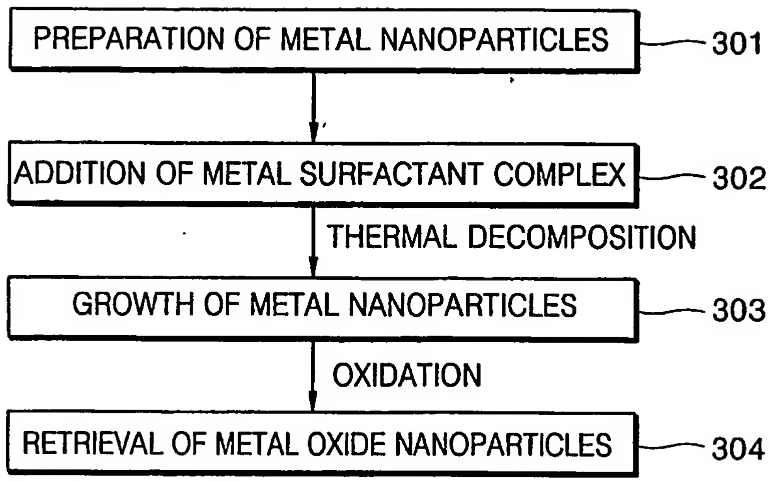

PREPARATION OF METAL NANOPARTICLES
301
ADDITION OF METAL SURFACTANT COMPLEX
302
THERMAL DECOMPOSITION
GROWTH OF METAL NANOPARTICLES
303
OXIDATION
RETRIEVAL OF METAL OXIDE NANOPARTICLES
304

FIG. 4

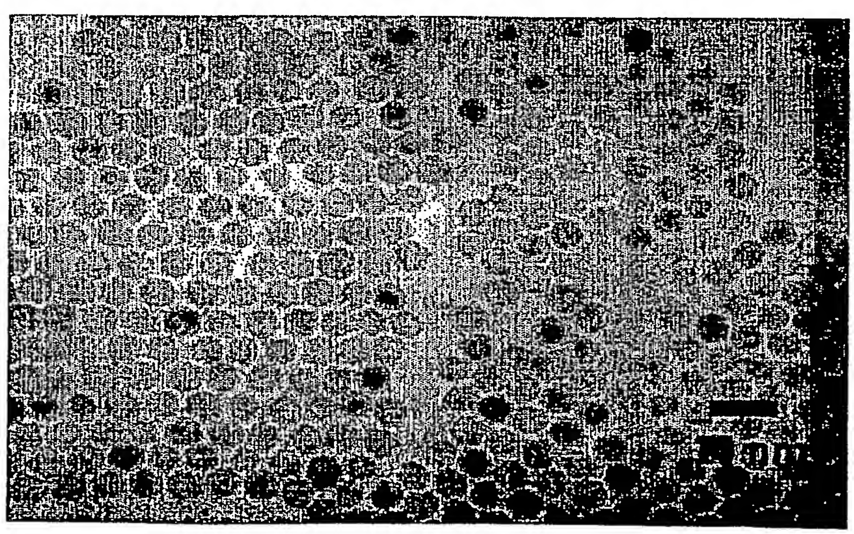


FIG. 5

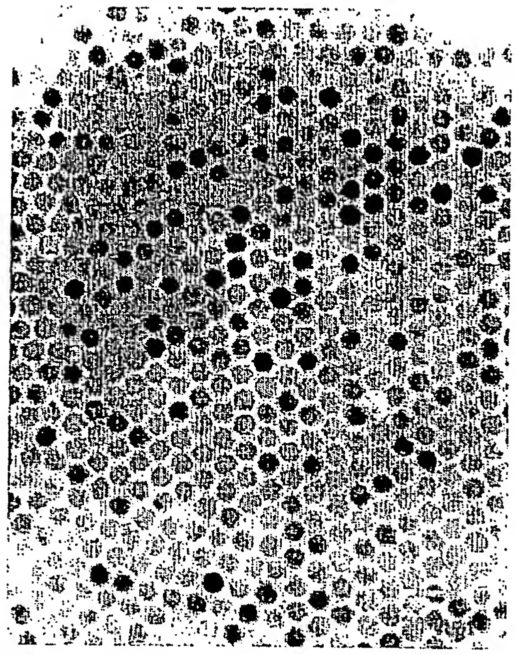


FIG. 6

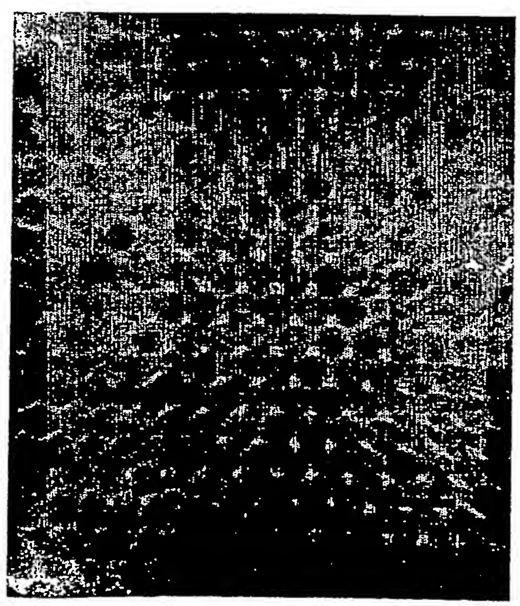


FIG. 7

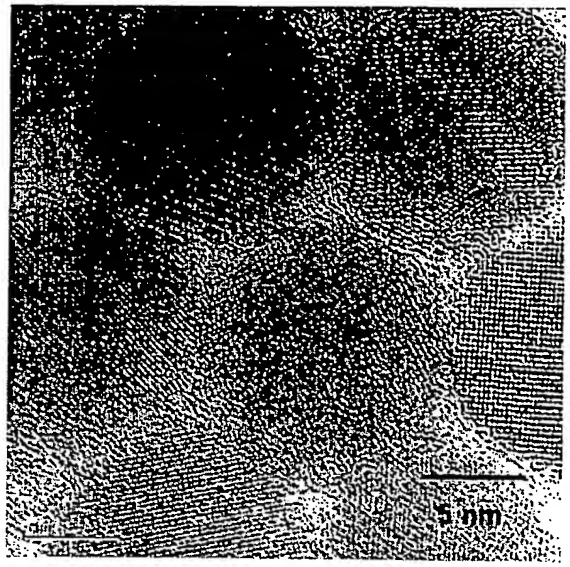


FIG. 8

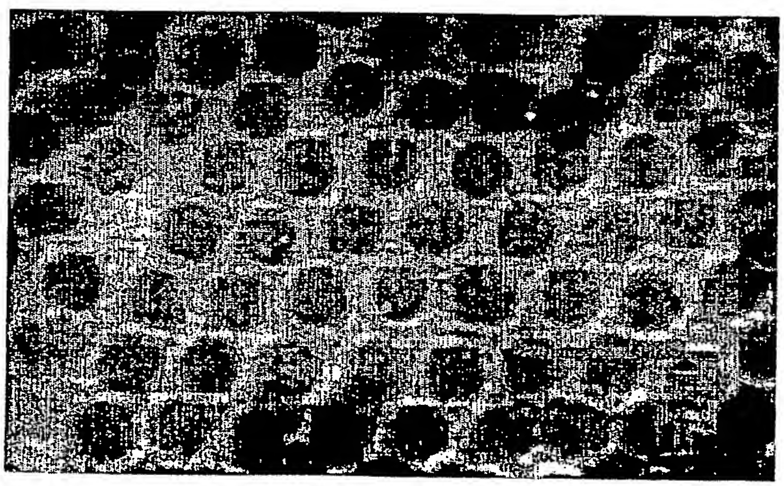


FIG. 9

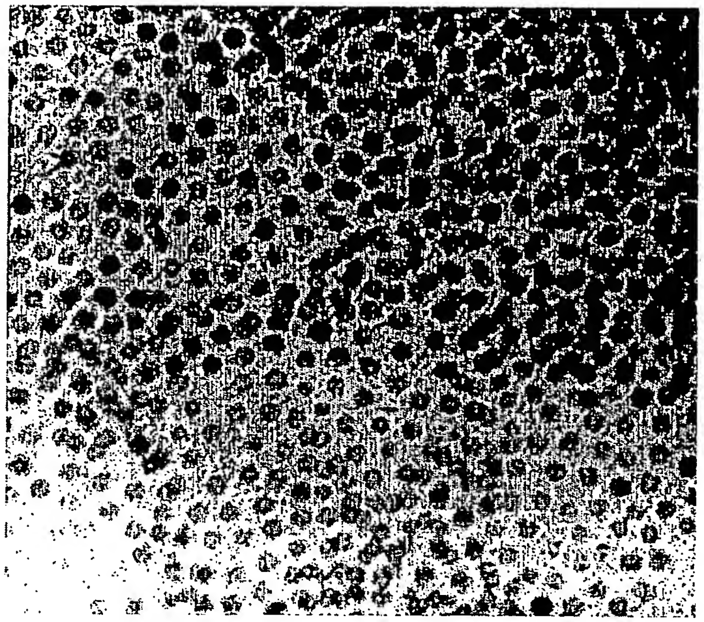


FIG. 10

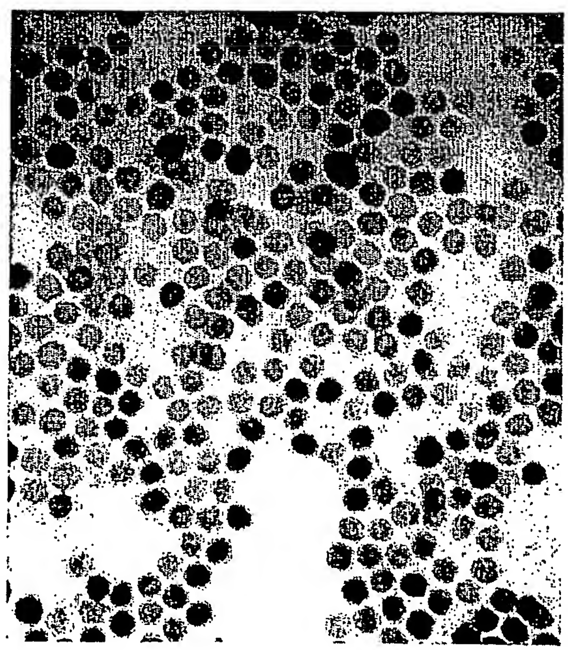


FIG. 11

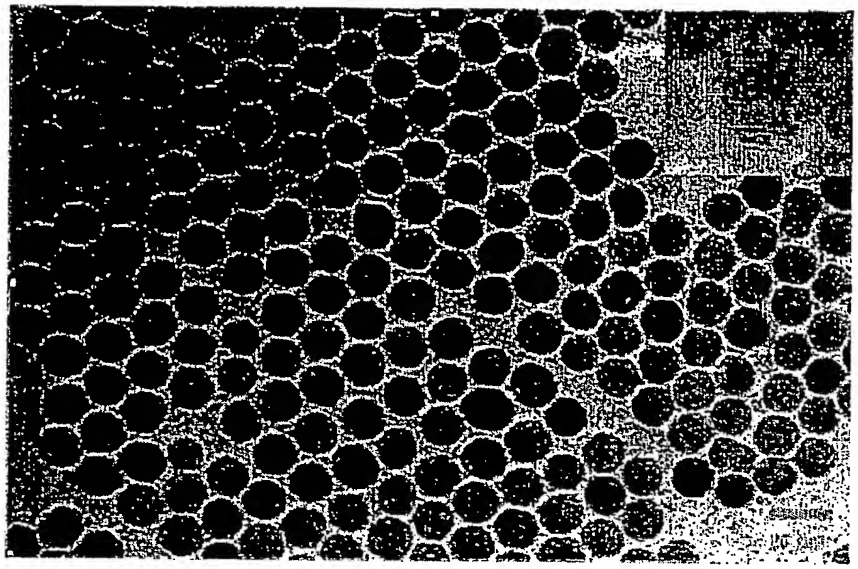


FIG. 12

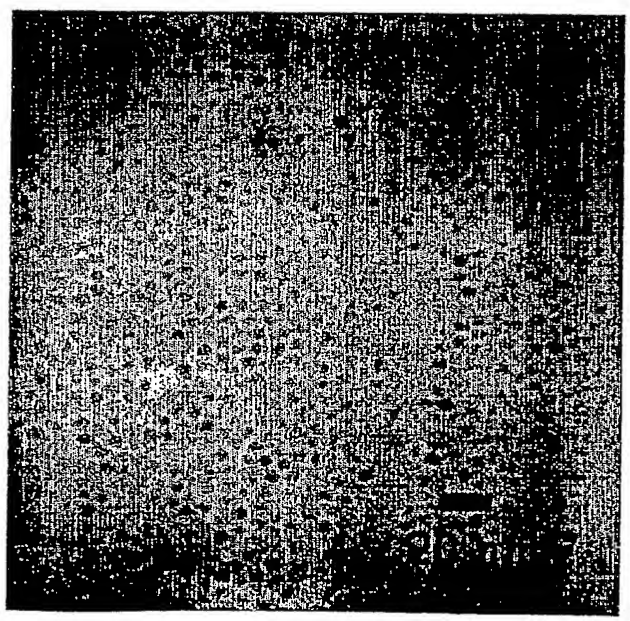


FIG. 13

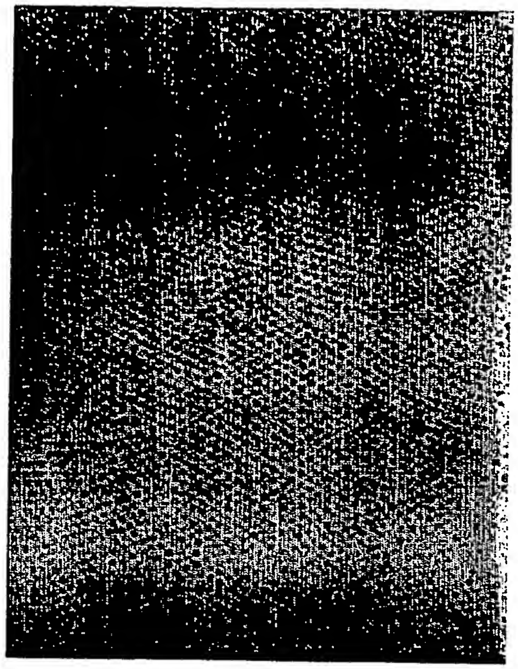


FIG. 14

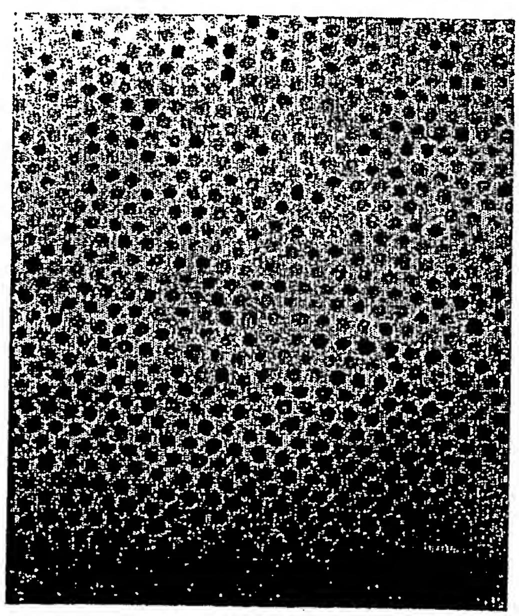


FIG. 15

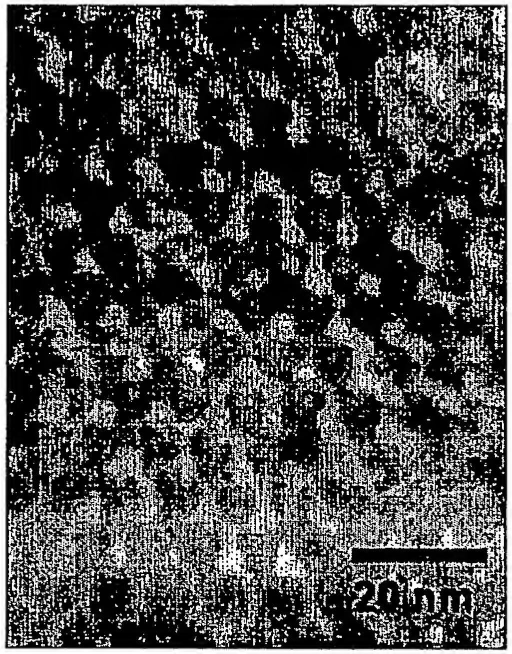


FIG. 16

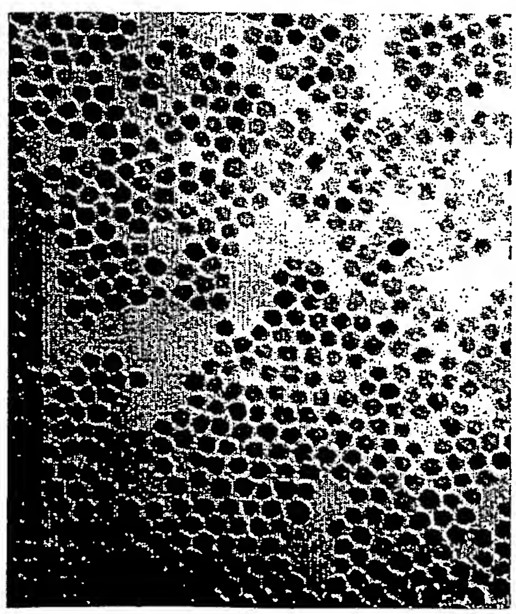
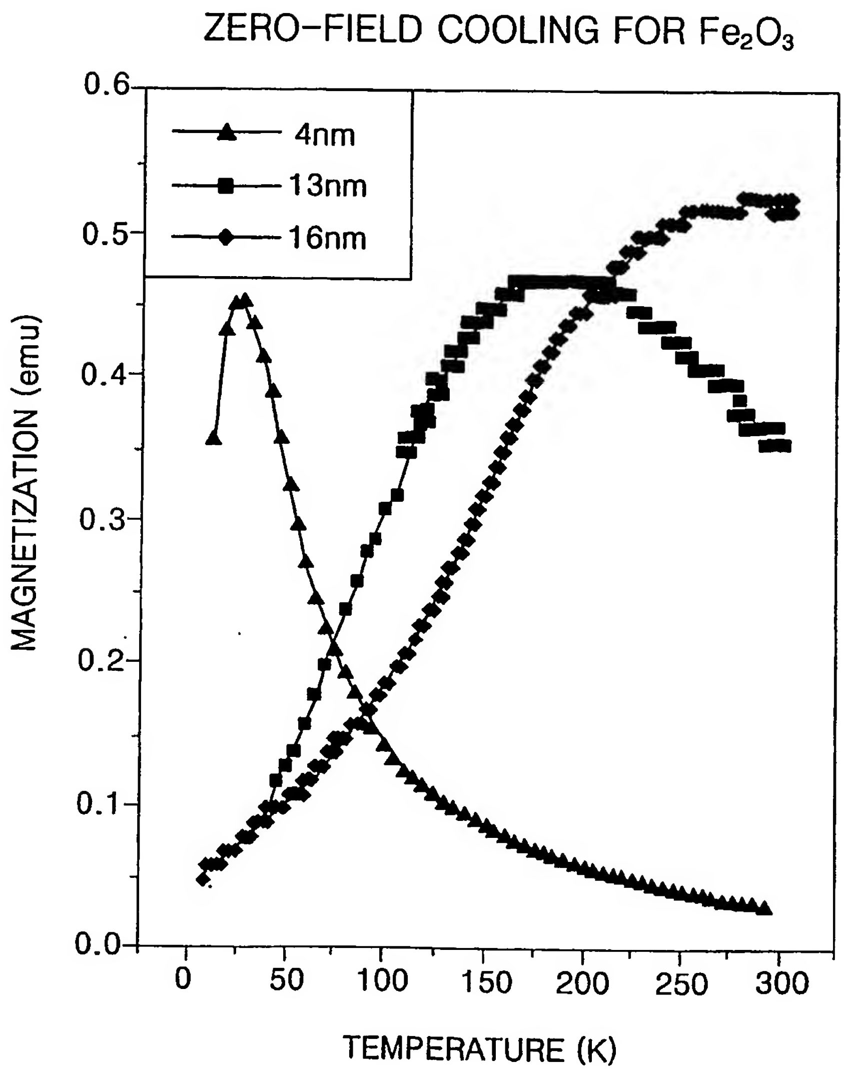


FIG. 17


ZERO-FIELD COOLING FOR Fe_2O_3
4nm
13nm
16nm
MAGNETIZATION (emu)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0
50
100
150
200
250
300
TEMPERATURE (K)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR02/00101

A. CLASSIFICATION OF SUBJECT MATTER

IPC7 B82B 3/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 B82B 3/00, B22F 9/16

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the intertnational search (name of data base and, where practicable, search terms used)

KIPASS, USP "METALLIC NANO*, SURFACTANT, METALLIC PRECURSOR"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6,268,014A (Chris Eberspacher; Karen Lea Pauls) 31 Jul. 2001(31. 7. 2001) See the whole document	1-19
A	US 5,958,361A (Regents of the University of Michigan) 28 Sep. 1999 (28. 9. 1999) See the whole document	1-19
A	US 5,759,230A (The United States of America as represented by the Secretary of the Navy) 2 Jun. 1998(2. 6. 1998) See the whole document	1-19

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevence

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevence; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevence; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 JULY 2002 (12.07.2002)	15 JULY 2002 (15.07.2002)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
920 Dunsan-dong, Seo-gu, Daejeon 302-701,
Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

JWA, Seung Kwan

Telephone No. 82-42-481-5560

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR02/00101

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6,268,014A	31. 7. 2001	WO 99/17889	15. 4. 1999
US 5,958,361A	28. 9. 1999	NONE	
US 5,759,230A	2. 6. 1998	NONE	